Desulfurization of liquid fuels by extraction and sulfoxidation using H_2O_2 and $[CpMo(CO)_3R]$ as catalysts

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ABSTRACT

Efficient and recyclable liquid–liquid extraction and catalytic oxidative desulfurization (ECODS) systems for the removal of refractory sulfur compounds from liquid fuels are reported that use the cyclopentadienyl molybdenum tricarbonyl complexes $[CpMo(CO)_3Me]$ (**1**), $[CpMo(CO)_3(CH_2-pC_6H_4-CO_2Me]$ (**2**) and $[CpMo(CO)_3CH_2COOH]$ (**3**) as catalyst precursors. An ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, was used as both extractant and reaction medium, entrapping the active homogeneous Mo^{VI} catalysts that are formed in situ under the operating catalytic conditions (aqueous H_2O_2 as oxidant, 50 °C). The high sulfoxidation activity of the catalyst formed from **1** was largely responsible for enabling > 99% desulfurization within 1 h of a model oil containing 1-benzothiophene, dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (2000 ppm S). The IL/catalyst phase could be repeatedly recycled with no loss of desulfurization efficiency. By sequentially performing extractive desulfurization and ECODS steps, 83–84% sulfur removal was achieved for untreated real diesel and jet fuel samples with initial sulfur contents of ca. 2300 and 1100 ppm, respectively.

1. Introduction

The desulfurization of transportation fuels is an important process in safeguarding the environment since the combustion of sulfur-containing fuels in motorized vehicles can contribute in a major way to SO_x air pollution [1]. Desulfurization techniques that do not use hydrogen (as in conventional hydrodesulfurization (HDS) processes) have been developed through mutual collaboration between academia and industry [1,2]. A high number of recent publications have focussed on the production of ultra clean fuels through oxidative desulfurization (ODS) technology, which is purported to avoid some of the problems inherent in HDS processes currently applied in the refining industry [3]. ODS allows the efficient and selective removal of aromatic and cyclic sulfur compounds by the combination of oxidation and extraction under mild conditions (low temperatures and no H_2 consumption) [1].

Many different organic polar solvents have been used as extractants in ODS. However, room temperature ionic liquids (RTILs) have stood out due to their unique physical properties such as non-volatility, high polarity, good thermal and chemical stability, non-flammability and capacity to be recycled [4–6]. Imidazolium RTILs have frequently been employed due to their high stability towards oxidation [7–10].

In the oxidative step of an ODS process the sulfur compounds are oxidized to the corresponding sulfoxides and/or sulfones using a selective oxidant in the presence of a suitable catalyst. The oxidation of sulfur compounds has been studied most frequently using hydrogen peroxide, organohydroperoxide (e.g. tert-butylhydroperoxide, TBHP) and peracid oxidants [3,11,12]. However, sulfur removal under environmentally friendly conditions demands the use of green oxidants, mainly molecular oxygen (O_2) [13–15] or hydrogen peroxide (H_2O_2) [16]. The latter is the most attractive oxidant to apply in ODS due to its ready availability and high concentration of active oxygen (47%), yielding only water as by-product [3,11,16].

To improve the performance of the ODS process, both in terms of selectivity and efficiency, various families of catalysts have been explored and developed for the oxidation of sulfur compounds with H_2O_2, including, for example, molybdenum or tungsten-containing polyoxometalates (POMs) [17–25], titanium micro/mesoporous silica materials [26–28], activated carbon [29], and oxometal complexes [30–32]. Molybdenum lies at the epicentre of oxygen atom transfer chemistry and Mo complexes are recognized as some of the most

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selective catalysts for the oxidation of various sulfides. However, the high efficiency of the Mo complexes is in many cases dependent on the use of less sustainable oxidants such as organohydroperoxides [33,34]. Several studies have nevertheless successfully combined Mo complexes with H_2O_2 for efficient sulfoxidation [35–41].

During the last fifteen years or so, organometallic oxo complexes of the type [Cp'MoO$_2$X] (Cp' = η^5-C$_5$R$_5$, R = H, alkyl, ansa-bridge; X = halide, alkyl, ansa-bridge) have emerged as excellent oxidation catalysts following the finding that the corresponding tricarbonyl complexes [Cp'Mo(CO)$_3$X] can serve as convenient synthetic/catalyst precursors [42]. A great variability of molecular catalysts can be obtained by derivatization of the cyclopentadienyl ring and/or introduction of different Mo-bonded groups X [43]. However, there are only a few reports on the use of [Cp'Mo(CO)$_3$X]/H_2O_2 systems in the oxidation of sulfides [44,45]. DFT mechanistic studies for sulfide and sulfoxide oxidation using the complex [CpMo(CO)$_3$Cl] (Cp = η^5-C$_5$H$_5$) indicated that the peroxo complex [CpMoO(O$_2$)Cl] forms via the dioxo complex [CpMoO$_2$Cl], which is readily formed from the tricarbonyl precursor in the presence of the oxidant ROOH (R = H, Me) [46]. The calculations revealed that sulfide to sulfoxide (or sulfoxide to sulfone) oxidation proceeds by external nucleophilic attack of the substrate to the peroxide which is activated through Mo–O coordination.

To the best of our knowledge there are no reports describing the use of [Cp'Mo(CO)$_3$X\] complexes in ODS processes. Here, we present the application of three different [Cp'Mo(CO)$_3$X] complexes in combined oxidation-extraction systems for the ODS of model and untreated real diesel and jet fuel. [CpMo(CO)$_3$X]@RTIL systems are shown to be recyclable for several consecutive cycles without loss of efficiency.

2. Experimental section

2.1. Materials and methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: Dibenzothiophene (Sigma-Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), n-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich, ≥98%), ethyl acetate (Fischer Chemical, analytical grade), diethyl ether (Merck), dimethylformamide (Fischer), 70 wt.% tert-butylhydroperoxide in water (Sigma-Aldrich) and 30% w/v hydrogen peroxide (Sigma-Aldrich). Untreated diesel and jet fuel samples containing 2300 and 1100 ppm S, respectively, were supplied by Galp Energia.

Complex [CpMo(CO)$_3$Me] (**1**) was synthesized by the reaction of Na[CpMo(CO)$_3$] with MeI [47]. Reaction of NaCp with Mo(CO)$_6$, followed by addition of 2-chloroacetamide, yielded the complex [CpMo(CO)$_3$CH$_2$COONH$_2$], which was then hydrolyzed to give [CpMo(CO)$_3$CH$_2$COOH] (**3**) [48]. Addition of 4-(bromomethyl)benzoate to Na[CpMo(CO)$_3$] resulted in the formation of [CpMo(CO)$_3$(CH$_2$-pC$_6$H$_4$-CO$_2$Me] (**2**) [49]. Detailed characterization data of the complexes is described in Supplementary Data.

2.2. Oxidative desulfurization of a model diesel

The ODS reactions were carried out under atmospheric pressure, using a borosilicate reaction vessel (5 mL) loaded with a magnetic stirring bar and immersed in a thermostated oil bath at 50 °C. A model diesel with a sulfur concentration of 2000 ppm was prepared by the dissolution in equal parts of dibenzothiophene (DBT), 1-benzothiophene (BT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in n-octane.

The conditions applied during the ODS experiments resulted from the evaluation of several parameters using a biphasic ODS system. The evaluated parameters were: nature of extraction solvent (methanol, MeCN, [BMIM]PF$_6$ or [BMIM]BF$_4$), volume of extraction solvent (0.750, 0.375 and 0.250 mL), type of oxidant (TBHPaq or H_2O_2), amount of H_2O_2 (0.60, 0.30, 0.22 and 0.15 mmol), and amount of catalyst **1** (10, 20 and 30 μmol).

The ODS reactions composed of a biphasic liquid-liquid system combine extraction and catalytic oxidation. Before addition of H_2O_2, an initial extraction of sulfur compounds present in the model diesel was performed by vigorously stirring the model diesel/extractant mixture for 10 min at 50 °C. After this stage, 30% aq. H_2O_2 (0.30 mmol; H_2O_2/S molar ratio = 6) was added to initiate the catalytic stage.

The periodic quantification of sulfur content by GC analysis was executed by taking aliquots with a microsyringe directly from the model diesel phase during the ODS reactions. In a typical procedure, a standard (tetradecane) was used to dilute the aliquot removed. For the recyclability tests, the model diesel phase was removed at the end of each cycle and the extractant phase was either reused immediately with no further treatment (cycles denoted "reused") or washed with a mixture of ethyl acetate and diethyl ether (1:1 v/v) to remove the sulfur-containing compounds (cycles denoted "recycled"). The consecutive cycles were performed under the same experimental conditions through the addition of fresh samples of model diesel and oxidant. Sulfur analyses were performed with a Bruker 430-GC-FID gas chromatograph, using a Supelco capillary column SPB-5 (30 m x 250 μm id.; 25 μm film thickness) and hydrogen as carrier gas (55 cm^3 s^{-1}).

2.3. Oxidative desulfurization of untreated real liquid fuels

The untreated real diesel and jet fuel samples were desulfurized maintaining the model diesel reaction proportions (H_2O_2/S/catalyst) at 50 °C for 2 h using [CpMo(CO)$_3$Me] (**1**) as catalyst precursor. Some initial extraction studies were performed with MeCN and dimethylformamide (DMF) for 30 min at 50 °C in the case of jet fuel and 70 °C for diesel. The analysis of sulfur content in the treated diesel was performed by Galp Energia using ultraviolet fluorescence test method (ISO 20846), using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry (ISO 8754), using a OXFORD LAB-X, LZ 3125.

3. Results and discussion

3.1. Desulfurization of a model diesel

A multicomponent model diesel containing 2000 ppm S was prepared by dissolution of DBT, BT, 4-MDBT and 4,6-DMDBT in n-octane. In a typical ODS process, the catalyst precursor of the type [CpMo(CO)$_3$R] was added to the extraction solvent, followed by addition of the model diesel to give a biphasic system. This mixture was stirred for 10 min at 50 °C to perform an initial extraction where a certain amount of the sulfur compounds present in the model diesel phase was transferred to the IL phase. After this, aq. H_2O_2 was added to the system to initiate the metal-catalyzed oxidation of the extracted sulfur compounds, which promotes ongoing extraction of the diesel phase by decreasing the concentration of non-oxidized sulfur compounds in the extractant phase (Scheme 1). It is noteworthy that no desulfurization of the model diesel was observed after the initial extraction stage in the presence of H_2O_2 and absence of catalyst.

3.1.1. Optimization study

With the objective of optimizing the ODS conditions, the influence of some experimental parameters on the removal of sulfur compounds from the multicomponent model diesel was investigated, using complex [CpMo(CO)$_3$Me] (**1**) as catalyst. Among the evaluated parameters were the type of extraction solvent (methanol, MeCN and two different imidazolium RTILs - [BMIM]PF$_6$ and [BMIM]BF$_4$), the extraction solvent/model diesel/volume ratio (1:1, 0.5:1, 0.3:1), the type and amount
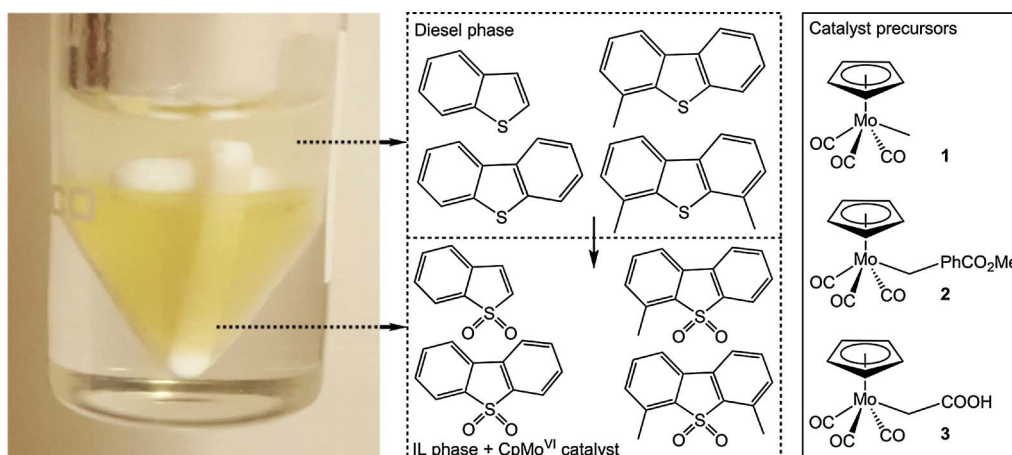
Scheme 1. Photograph of a typical ODS reaction mixture and schematic representations of the $[CpMo(CO)_3R]$ catalyst structures and the ODS process.

of oxidant (TBHPaq or H_2O_2; 0.60, 0.30, 0.22 and 0.15 mmol of H_2O_2) and catalyst **1** amount (10–30 μmol).

The extraction capacity as reaction medium of four different solvents were analyzed for the ODS process using 0.75 mL of extraction solvent and 0.75 mL of the model diesel with a reaction temperature of 50 °C in the presence of 10 μmol of catalyst **1** and 0.60 mmol of H_2O_2. The influence of each solvent (methanol, MeCN, [BMIM]PF$_6$ and [BMIM]BF$_4$) on desulfurization is illustrated in Fig. 1. Regardless of the extraction solvent applied, during the initial extraction stage the desulfurization of each sulfur compound followed the order BT > DBT > 4-MDBT > 4,6-DMDBT. This order is related with the molecular diameter and geometry of each sulfur compound, as well as with their solubility in different polar solvents [50]. Considering all of the sulfur compounds present in the model diesel, the initial extraction performance followed the order MeCN > [BMIM]BF$_4$ > [BMIM]PF$_6$ > MeOH. However, in the oxidative catalytic stage, which is initiated by the addition of H_2O_2 to the ODS system, a near complete desulfurization of the model diesel was achieved in the presence of [BMIM]PF$_6$ after 5 h of reaction at which point only 35 ppm of BT persisted in the oil phase. This difficulty in removing BT is usually accounted for as an effect of the electron density at the S atom [24,51–53]. For equal reaction time (5 h), the desulfurization efficiency of each extraction solvent followed the order methanol (83.1%) < [BMIM]BF$_4$ (85.3%) < MeCN (90.9%) < [BMIM]PF$_6$ (98.0%). Therefore, [BMIM]PF$_6$ proved to be the preferred extraction solvent and reaction medium for chemical oxidation, despite its low extraction efficiency during the extraction stage when compared to MeCN. This behaviour has been noted previously for desulfurization systems and can be associated with the water-immiscibility of [BMIM]

PF$_6$, which results in the formation of a triphasic system (diesel/H_2O_2/IL) in the presence of aqueous H_2O_2 and model diesel [7,17].

The extraction solvent/diesel volume ratio is an important parameter in an ODS process mainly due to the high cost of ILs. To minimize these drawbacks and favour application of ILs in ODS processes, it is necessary decrease the dosage of IL. To investigate the effect of the [BMIM]PF$_6$/diesel volume ratio, a comparative study was performed in which [BMIM]PF$_6$/diesel volume ratios of 1:1, 0.5:1 and 0.3:1 were tested, using 10 μmol of catalyst **1** in the presence of 0.60 mmol of H_2O_2 at 50 °C. Figure S1 in the Supplementary Data displays the desulfurization profiles obtained for different volume ratios of [BMIM]PF$_6$/diesel. The consequences of a decrease in the volume ratio are mainly evident during the initial extraction stage, where a higher transfer of sulfur compounds from the model diesel to the IL was obtained for the 1:1 ratio. The extraction yield decreased linearly with the decrease in the volume ratio (from 42.7% to 23%). These results were expected since a higher IL volume results in an improvement of the transfer of non-oxidized sulfur compounds from the model diesel to the IL phase. However, during the catalytic stage, the influence of the volume ratio was less perceptible since a complete desulfurization was obtained after 6 h of ODS reaction using all [BMIM]PF$_6$/diesel volume ratios. The different effects of IL/model diesel volume ratios observed during the initial extraction and catalytic stages can be related with the sulfur Nernst partition coefficients that are more sensitive to chemical extraction than purely physical extraction [54,55]. In other words, the similar catalytic efficiency observed for each [BMIM]PF$_6$/diesel system must be due to the oxidation of the sulfur compounds, since the oxidized species possess a polarity comparable to the IL, facilitating the desulfurization through the continued transfer of sulfur compounds from the model diesel to the IL phase during the ODS process, independent of the [BMIM]PF$_6$/diesel volume ratios.

The influence of different amounts of catalyst **1** (10, 20 and 30 μmol) was investigated in desulfurization of the model diesel, maintaining all the other reaction conditions constant ([BMIM]PF$_6$/model diesel volume ratio = 0.3:1, 0.60 mmol of H_2O_2 and 50 °C) (Figure S2 in the Supplementary Data). The efficiency of the ODS processes was similar using 10 or 20 μmol of the catalyst since these presented similar desulfurization profiles. A slight increase of desulfurization is observed using 30 μmol of catalyst, mainly during the first 2 h of reaction. After 4 h a complete desulfurization was observed in the presence of 30 μmol of catalyst, while 81 and 19 ppm of S were still present in the model diesel using 10 and 20 μmol catalyst, respectively.

Using the best experimental conditions observed so far ([BMIM]PF$_6$/model diesel volume ratio = 0.3:1, 30 μmol of catalyst **1** and 50 °C), the amount of 30% aq. H_2O_2 was varied in the range 0.15–0.60 mmol. Fig. 2 displays the desulfurization profiles of the
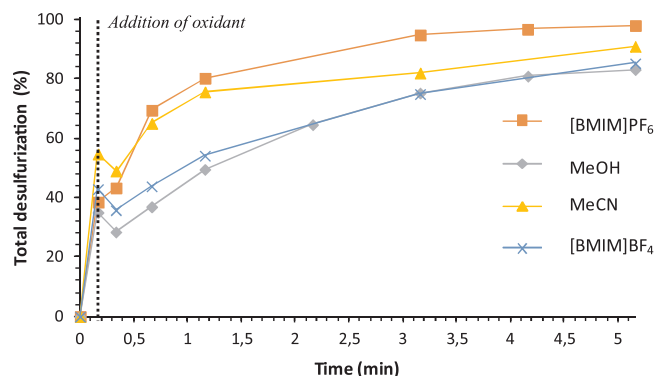
Fig. 1. Desulfurization of a multicomponent model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (10 μmol) as precatalyst in the presence of different extraction solvents, at 50 °C and using 0.60 mmol of H_2O_2 oxidant.
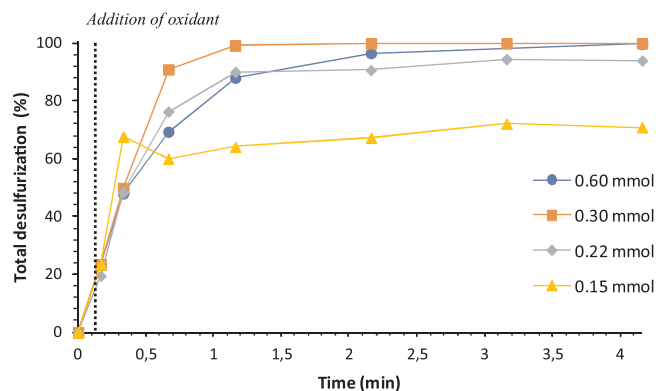
Fig. 2. Desulfurization of a multicomponent model diesel (2000 ppm S) at 50 °C using [CpMo(CO)₃Me] (**1**) (30 μmol) as precatalyst, [BMIM]PF₆ as extraction solvent (0.25 mL), and different amounts of H₂O₂ as oxidant.

multicomponent model diesel using different amounts of oxidant (0.60, 0.30, 0.22 and 0.15 mmol). The highest desulfurization of the model diesel was obtained using 0.30 mmol of H_2O_2, where a complete desulfurization was achieved after 2 h of ODS reaction. It is noteworthy that at 1 h, only 9 ppm of sulfur was present in the model diesel. The slower desulfurization registered with the higher amount of H_2O_2 (0.6 mmol) can be related with a decrease in contact area between the model diesel and the IL phase containing the catalyst since the aqueous H_2O_2 phase is located between these two phases [17].

The ECODS process was also studied at 25 °C and the desulfurization profile was compared with the one obtained at 50 °C under the same experimental conditions (Figure S3 in the Supplementary Data). The desulfurization efficiency at room temperature is lower than at 50 °C. Thus, while the initial extraction was similar at both temperatures, differences in efficiency were observed during the catalytic oxidative step. After 1 h of oxidation only 75% of desulfurization was achieved at 25 °C instead of near complete desulfurization at 50 °C.

Since tert-butylhydroperoxide (TBHP) is frequently applied as a successful oxidant in oxidative catalysis together with molybdenum complexes as catalysts, desulfurization of the model diesel using aqueous TBHP (TBHPaq) instead of H_2O_2 was examined, keeping the other parameters constant (reaction temperature of 50 °C, 30 μmol of precatalyst **1** and 0.3:1 (v/v) [BMIM]PF₆/model diesel). Fig. 3 shows that in the presence of H_2O_2 a complete desulfurization was reached after 1 h of catalytic reaction, while in the presence of TBHPaq the total desulfurization levelled off at about 84% after 2 h of reaction. The different rates observed during the catalytic stage for each oxidant can be related with the possibility of specific catalytic pathways for H_2O_2 and TBHPaq. However, both ODS systems presented a yellow colored phase after addition of H_2O_2 or TBHPaq, so probably the active species
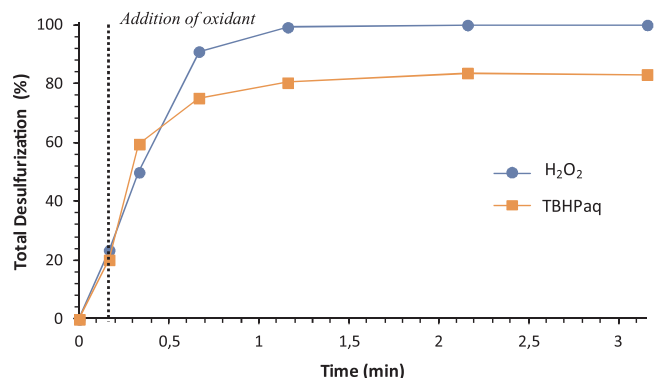

Fig. 3. Desulfurization of a multicomponent model diesel (2000 ppm S) at 50 °C using [CpMo(CO)₃Me] (**1**) (30 μmol) as precatalyst, [BMIM]PF₆ as extraction solvent (0.25 mL), and H₂O₂ or TBHPaq (0.30 mmol) as oxidant.
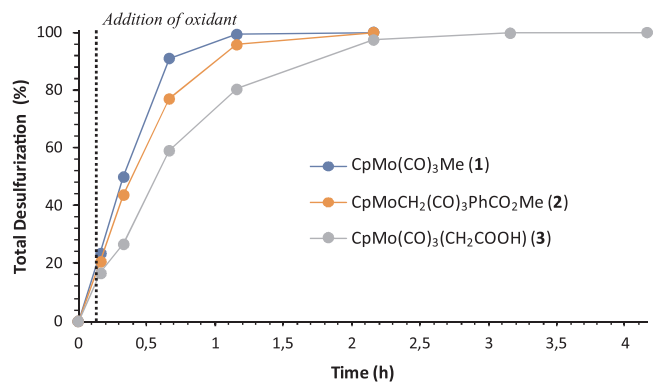

Fig. 4. Desulfurization profile of a multicomponent model diesel using different catalyst precursors (**1**, **2** and **3**) in the presence of [BMIM]PF₆ as extraction solvent (0.25 mL) and H₂O₂ (0.30 mmol) as oxidant, at 50 °C.

are similar, since the yellow colour is generally associated with the presence of active oxoperoxo-molybdenum(VI) species (Scheme 1) [7,49].

3.1.2. Comparison of [CpMo(CO)₃R]@[BMIM]PF₆ efficiency

After optimization of the ODS conditions, the desulfurization performance of other [CpMo(CO)₃R] (R = CH₂PhCO₂Me (**2**) and CH₂COOH (**3**)) catalyst precursors was investigated (Scheme 1). The desulfurization profile for each catalyst was compared with that for the previous catalyst **1** (R = Me) using the same molar amount (30 μmol) as well as the same optimized experimental conditions, i.e. 0.3:1 [BMIM]PF₆/model diesel volume ratio, 0.30 mmol of H_2O_2, and a reaction temperature of 50 °C (Fig. 4). As expected the initial extraction obtained in the presence of the various catalysts was similar (around 20%) since the extraction stage is generally only influenced by the extraction solvent efficiency. During the catalytic stage, which begins after addition of the oxidant, different desulfurization efficiencies were observed for each catalyst. A completely desulfurized model diesel was obtained in the presence of precatalyst **1** after 2 h of ODS reaction (at 1 h only 8 ppm of sulfur remained in the model diesel), while at the same reaction time precatalyst **2** led to 95% desulfurization and precatalyst **3** to 80% desulfurization. Precatalyst **3** displayed the poorest ODS performance with a reaction time of 4 h being required to obtain sulfur-free model diesel. Thus, the reactivity order of the catalysts was **1** > **2** > **3**. The main reason for the different catalytic activity observed may arise from distinct steric hindrance effects promoted by the different -sized R groups present in [CpMo(CO)₃R] catalysts. This effect will promote a different interaction rate between the catalyst and the oxidant to form the active catalytic species, i.e. oxoperoxo-molybdenum(VI) complexes (Scheme 1). Comparing the catalytic activity of complexes **2** and **3**, the presence of a substituent on the phenyl ring in its molecular structure may lead to activation of the phenyl ring, which may affect the catalytic efficiency [45]. According to the literature, complexes of the type [CpMo(CO)₃R] can be oxidized into the corresponding dioxo [CpMoO₂R] and oxoperoxo [CpMoO(O₂)R] derivatives using H_2O_2 or TBHPaq oxidants. The [CpMoO₂R] complexes are intermediates in the formation of [CpMoO(O₂)R] both CpMo(VI) species are recognized as being active catalysts for oxidation reactions [46]. The oxoperoxo complexes present a characteristic yellow colour as observed in this work (Scheme 1).

3.1.3. [CpMo(CO)₃R]@[BMIM]PF₆ recyclability and reutilization

Recyclability and reutilization tests were performed for several ODS cycles using the complexes [CpMo(CO)₃R] as precursors to homogeneous catalysts. Since the catalysts could not be separated from the ODS systems, the extraction phase containing the catalyst entrapped in [BMIM]PF₆ was reused and recycled for at least five consecutive ODS cycles (Fig. 5, and Figures S4 and S5 in the Supplementary Data). After
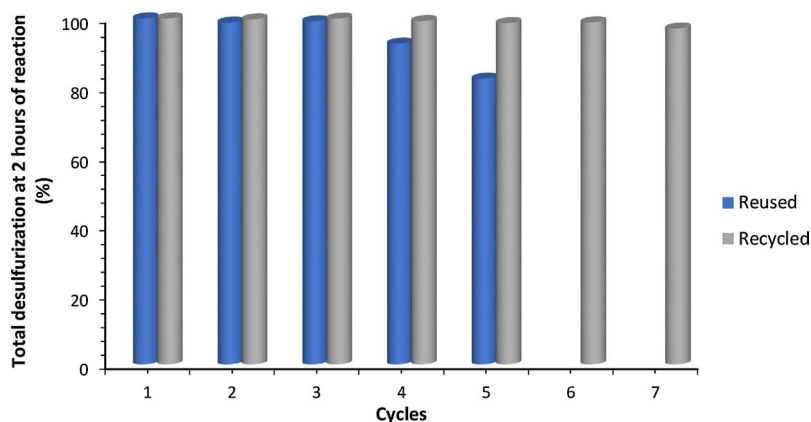
Fig. 5. Desulfurization data for five and seven consecutive reused and recycled ODS cycles, respectively, using [CpMo(CO)$_3$Me] (**1**) as catalyst precursor, a multicomponent model diesel and [BMIM]PF$_6$ with a volume ratio of 1:0.3, at 50 °C with H$_2$O$_2$ (0.30 mmol) as oxidant.

removal of the model diesel phase at the end of each cycle, different procedures were performed for the "reused" and "recycled" series of reactions. In the reused ODS tests, a fresh portion of model diesel was added to the IL phase and, after completing the initial extraction stage, fresh oxidant was added to start the catalytic stage. In the recycled ODS tests, the IL phase was washed with a mixture of ethyl acetate and diethyl ether (1:1 v/v) to remove the sulfur-containing compounds resulting from the extraction/oxidation reactions, and then fresh portions of model diesel and oxidant were added sequentially as carried out for the reused ODS tests. The results showed that for all three precatalysts **1-3**, both the reused and recycled ODS systems were stable up to and including the third cycle. However, during the fourth and fifth cycles the reused systems generally display a loss in efficiency, especially noticeable for the most active precursor **1**. This fall-off in desulfurization efficiency probably occurs due to the saturation of the extraction phase with the oxidized sulfur compounds in the consecutive cycles, blocking the extraction of new portions of sulfur compounds from the model diesel, thus promoting a decrease in the number of sulfur compounds oxidized. Accordingly, the washing treatment prevents the saturation of sulfur compounds in the IL phase, promoting a continuous extraction/oxidation for various ODS cycles as shown in Fig. 5 where near-complete desulfurization is maintained for 7 cycles. The water content arising from the aqueous oxidant is another important parameter that contributes to the decrease in efficiency of the reused process, since the aqueous phase located between the model diesel and [BMIM]PF$_6$ phases increases in volume between reused consecutive cycles. In the recycling process the water arising from the oxidant is removed by the cleaning process performed with the solvent mixture. The analysis of the ethyl acetate/diethyl ether mixture used to clean the extraction phase of ECODS process indicated the presence of the same oxidized sulfur products (corresponding sulfones of BT, DBT, 4-MDBT and 4,6-DMDBT) as identified in the [BMIM]PF$_6$ phase.

3.2. Desulfurization of real liquid fuels

The catalyst that revealed the highest efficiency ([CpMo(CO)$_3$Me] (**1**)) was used in oxidative desulfurization of untreated real liquid fuels supplied by Galp Energia (a diesel with ca. 2300 ppm S and a jet fuel sample with ca. 1100 ppm S). The main families of sulfur compounds present in this untreated diesel were benzothiophene and dibenzothiophene derivatives as previously reported [19]. The desulfurization process of the untreated real diesel and jet fuel was performed using the same conditions applied for the ODS of the model diesel. To verify the effect of the extraction time, extraction tests using 1:1 untreated diesel: MeCN were performed with durations of 5, 10 and 30 min. According to the results presented in Table 1, the extraction efficiency was not time dependent, since the sulfur content present in

the real diesel after the extraction was practically equal regardless of the time applied. However, maintaining the extraction time and using two different solvents, namely MeCN and DMF, revealed a better desulfurization efficiency using DMF (34.2%) than MeCN (17.8%). For desulfurization of the jet fuel, the best result was achieved in the presence of MeCN, which can be related with the polarity and the chemical composition of this fuel, mainly with the sulfur compounds here present.

The real diesel and jet fuel were further desulfurized through an oxidative step involving application of a biphasic fuel/[BMIM]PF$_6$ system in the presence of [CpMo(CO)$_3$Me] (**1**) and H$_2$O$_2$ at 50 °C. The oxidative desulfurization of the diesel with an initial extraction of 10 min (1910 ppm S) catalyzed by **1** allowed a decrease in sulfer content from 1910 to 372 ppm S. The desulfurization of the real diesel was more successful when MeCN was used as final extraction solvent. Referring to Table 1 it is evident that MeCN possesses higher extraction efficiency than DMF after the oxidation process, which is the opposite of that observed during the initial extractions. This behaviour can be related with a higher affinity of the sulfoxides/sulfones towards MeCN, while the non-oxidized species possess more affinity towards DMF. On the other hand, the final extraction time occurring after oxidation seemed to have an important influence on the desulfurization efficiency, since a longer final extraction allowed higher desulfurization. Using MeCN as final extractant the desulfurization efficiency increased from 74.4% to 83.8% upon increasing the extraction time from 10 to 30 min. In the case of jet fuel, the initial extractions with MeCN and DMF were similar with desulfurization efficiencies of 14.7% and 9.94%, respectively. When the catalytic oxidation using model diesel conditions was applied followed by final extraction with DMF and MeCN, jet fuels with low amounts of sulfur content were obtained (277 and 267 ppm, respectively). These results demonstrate that the oxidation is an important step for desulfurization of fuels, achieving better results when a conciliation of extraction and oxidation is achieved.

The remarkable high oxidation efficiency of the [CpMo(CO)$_3$Me] (**1**) catalyst is clarified when compared with other reported works for the oxidative desulfurization processes of real diesel using various homogeneous and heterogeneous metallic catalysts [7,19,56].

4. Conclusions

In summary, the efficient removal of benzothiophene derivatives from a multi-component model diesel as well as real diesel and jet fuel samples has been achieved by combining liquid-liquid extraction with an optimized ODS process that employs cyclopentadienyl molybdenum tricarbonyl complexes as precatalysts, an ionic liquid as solvent and extractant, and aqueous H$_2$O$_2$ as oxidant, under eco-sustainable conditions. A key finding is that the net sulfur removal levels are strongly

Table 1
Experiments performed for desulfurization of untreated real diesel and jet fuel, using the model diesel conditions.

Fuel	Catalyst	Extraction process[a]	Extraction time (min)	ODS process[b,c]	S content (ppm)	Desulfurization efficiency (%)
Diesel	–	MeCN	5	–	1920	16.5
		MeCN	10	–	1910	16.9
		MeCN	30	–	1890	17.8
		DMF	30	–	1513	34.2
	1	–	–	DMF[b]	1000	56.5
		–	–	MeCN[b]	1533	33.3
		MeCN	30	MeCN[b]	372	83.8
		MeCN	10	MeCN[c]	588	74.4
		MeCN	10	DMF[c]	521	77.3
		DMF	30	DMF[b]	384	83.3
Jet fuel	–	MeCN	30	–	938	14.7
	–	DMF	30	–	991	9.94
	1	–	30	DMF[b]	277	74.8
		MeCN	30	MeCN[b]	267	75.8

[a] Liquid-liquid fuel/organic solvent extraction of non-oxidized sulfur compounds during 30, 10 or 5 min at 70 °C.
[b] Oxidative desulfurization in a biphasic fuel/[BMIM]PF$_6$ system during 2 h using the same conditions applied for the model diesel with a final extraction with an organic solvent (MeCN or DMF) during 30 min.
[c] Oxidative desulfurization in a biphasic fuel/[BMIM]PF$_6$ system during 2 h using the same conditions applied for the model diesel with a final extraction with an organic solvent (MeCN or DMF) during 10 min.

influenced by the catalytic sulfoxidation activity which is not the same for the different catalyst precursors investigated. The results are consistent with previous experimental and theoretical studies that have indicated that [CpMo(CO)$_3$R] precatalysts react with the oxidant to give oxo-peroxo active species of the type [CpMoO(O$_2$)R] in which the Mo-bonded R group remains coordinated to the metal center, thereby influencing catalytic performance. This opens up the possibility of ODS optimization through ligand design and indeed such an approach has already been successful in optimizing [CpMo(CO)$_3$R] precatalysts for olefin epoxidation [43,57]. Further work in our laboratories will therefore focus on preparing a wider range of cyclopentadienyl molybdenum complexes and evaluating their performance in catalytic ODS processes.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.02.036.

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